

5 METAL REMOVAL AND RECOVERY BY LIQUID-LIQUID EXTRACTION

CLAIMS

We claim:

10

1. A process for the extraction metal ions from a dilute aqueous solution comprising:

15

a. contacting the aqueous solution with an extraction solution comprising a metal extractant for ions, a diluent, and a modifier at a pH below 6, wherein ions are extracted from the aqueous solution, and wherein the ratio of aqueous solution to extraction solution (A/E) is above about 4/1;

20

b. separating the contacted solutions into a loaded extraction solution phase containing the metal ions bound with an extractant-metal bond and a detoxified aqueous phase reduced in metal ion content; and

c. separating the phases.

25 2. The process according to Claim 1, wherein metal ions are stripped from the extraction solution phase.

3. The process according to Claim 1, comprising the additional step of adjusting the pH to less than 6 by adding a strong acid.

30 4 The process according to Claim 1, wherein the phases are separated via their mutual immiscibility and specific gravity difference.

5. The process according to Claim 1, wherein the oxometal ion is stripped from the extraction solution phase by increasing the solution pH, wherein the extractant-metal bond is broken, recovering the metal as an aqueous metal salt concentrate phase.

5

6. The process according to Claim 2, wherein the metal anions are stripped from the extraction solution phase by adding base.

7. The process according to Claim 2, wherein the loaded extraction  
10 solution is contacted with base and water to strip metal ion to form a regenerated extraction solution and a product aqueous solution, and wherein about 10 vol % to about 99 vol % of the product aqueous solution is recycled to be contacted by the loaded extraction solution, water and base.

15 8. The process according to Claim 7, wherein for metal ion stripping, the pH range is from about 11 to about 14.

9. The process according to Claim 7 wherein water is added in the stripping step at a rate sufficient to maintain a substantially constant aqueous  
20 metal salt concentrate or an aqueous metal salt concentrate within a selected range.

10. The process according to Claim 6, further comprising:

- 25 1. contacting the separated loaded extraction solution with base, water, and internally recycled product aqueous solution and mixing;
2. separating the mixture into a recycled extraction solution depleted in metal ion content and a product aqueous solution depleted in metal ion content;
3. recycling a portion of the product aqueous solution to step 1; and
- 30 4. separating another portion of the product aqueous solution from step 3 for metal ion recovery.

11. The process according to Claim 10, wherein the regenerated extraction solution is recycled to the contacting step of Claim 1.

12. The process according to Claim 1, wherein chromium is extracted from the aqueous solution.

13. The process according to Claim 1, wherein the extractant is a tertiary amine represented by the general formula,  $NR_1R_2R_3$ , where  $R_1$ ,  $R_2$ , or  $R_3$  may be the same or different and are selected from the group  $R_1 = C_1 - C_{18}$ ,  $R_2 = C_1 - C_{18}$ , and  $R_3 = C_1 - C_{18}$ , total Cn is 9 – 40 or represented by the general formula  $NR_1R_2R_3R_4$ , where  $R_1$ ,  $R_2$ ,  $R_3$ , or  $R_4$  may be the same or different and are selected from the group  $R_1 = C_1 - C_{18}$ ,  $R_2 = C_1 - C_{18}$ ,  $R_3 = C_1 - C_{18}$  and  $R_4 = C_0 - C_{18}$ , and total Cn is 9 – 40; and comprises about 0.5 to about 30 w% of the total extraction solution.

14. The process according to Claim 1, wherein Cr(VI) and Cr(III) are both extracted.

15. The process according to Claim 14, wherein the metal ion extractants comprise from about 0.5 to about 30 wt% of the extraction solution.

16. The process according to Claim 1, wherein the loaded extraction solution regeneration is achieved using a strong base to increase the pH.

17. The process according to Claim 3, wherein the strong acid is selected from the group consisting of as  $H_2SO_4$ ,  $HCl$ ,  $H_2PO_4$ ,  $CH_3SO_3H$ ,  $HNO_3$ , and  $HF$ .

18. The process according to Claim 1, wherein the aqueous solution is the effluent from surface finishing operations.

19. The process according to Claim 1, wherein the pH of the extraction and stripping circuits are automatically controlled.
20. The process according to Claim 1, wherein for anion extraction the pH  
5 range is from about 2 to about 5.
21. The process according to Claim 1, wherein the pH range is from about 2.5 to about 4.5.
- 10 22. The process according to Claim 1, wherein the A/E ratio is at about 4/1 to about 20/1.
23. The process according to Claim 1, wherein the A/E ratio is at about 6/1 to about 20/1.
- 15 24. The process according to Claim 1, wherein the A/E ratio is at about 8/1 to about 20/1.
25. The process according to Claim 1, wherein the diluent comprises an  
20 aliphatic or aromatic hydrocarbon, having about 5 to about 15 carbon atoms, and comprises from about 50 to about 99.5 wt% of the extraction solution.
26. The process according to Claim 1, wherein the modifier comprises a  
25 long chain aliphatic, straight or branched chain hydrocarbon alcohol and comprises from about 0 to about 20 wt% of the extraction solution.
27. The process according to Claim 1, wherein a mixer is used in the  
contacting and the mixer has a stirrer with a tip speed in the range of about 1.5 to about 7.5 m/sec and the residence time in the contacting ranges from  
30 about 0.1 to about 10 minutes.

28. A process for the simultaneous extraction of metal anion from an aqueous solution by means of ion pairing, and metal cation extraction by colloidal capture.

5 29. A process for the simultaneous extraction of metal anion (Cr(VI)) by ion pairing, and metal cation (Cr(III)) extraction by colloidal capture.

30. An apparatus for the extraction of metal anions from an aqueous solution comprising:

- 10 a. means for contacting the solution with an extraction solution comprising a metal extractant, a diluent, and a modifier, and mixing;
- b. means for separating the mixture into a loaded extraction solution containing the metal ion and a detoxified aqueous solution reduced in metal ion content;
- 15 c. means for separating the solutions; and
- d. means for recovering the metal ion from the extraction solution.

31. The apparatus according to Claim 30, wherein the means for recovering the metal ion from the extraction solution phase comprises:

- 20 1. means for contacting the loaded extraction solution with a base, and water and mixing;
2. means for separating the mixture into a regenerated extraction solution reduced in metal ion content and a product aqueous solution increased in metal ion content;
- 25 3. means for recycling a portion of the product aqueous solution from the means for separating to the means for contacting the loaded extraction solution with a base and water for further mixing; and
4. means for removing product aqueous phase from the means for separating for recovering the metal ion from the product aqueous
- 30 solution.